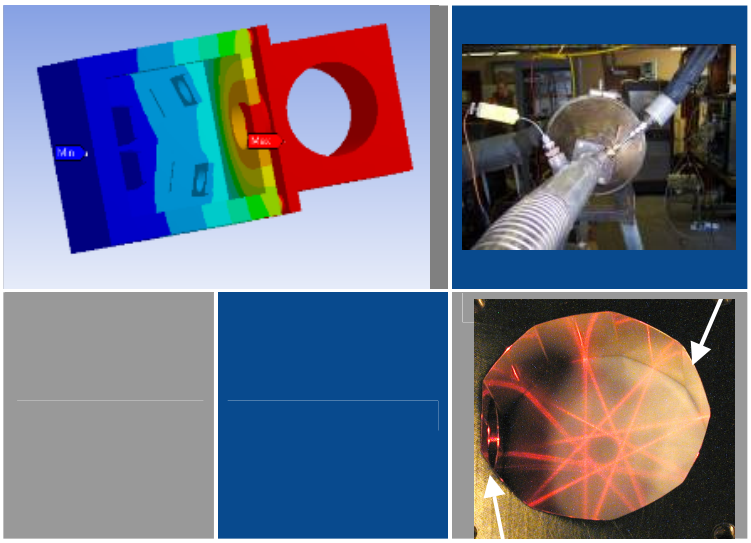
DE-FC26-03NT41968 FINAL REPORT

Real-Time, In Situ Sensor for Control of Ammonia Slip in SCR Installations



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Abstract

In this program, we proposed to demonstrate a compact, rugged, low-cost ammonia sensor with better than ±0.2 ppmv lower detection limit and resolution. Extensive design and trade studies indicated that this measurement could be made by exploiting the infrared absorbance of ammonia at 1527 nm to determine concentration. Key features of the design were 1) a electronically-tunable, wavelength-agile diode laser-pumped fiber laser, 2) a unique, low-cost folded path optical cell, and 3) an InGaAs photodiode (light detector). The sensor would be designed to make *in situ* measurements of ammonia in flue gas just downstream from the catalyst. The design proved robust and was able to operate at pressures in the range 1-3 atm and temperatures up to 500°C. With extensive signal processing, the sensor was able to make unambiguous ammonia measurements. But the signal processing degraded response time to almost 3 seconds and the measurement ambient conditions limited achievable resolution to about 20 ppmv ammonia. Extensive re-design, including a much longer optical path length and more robust real-time signal processing would be required to make sub-ppm measurements using this approach. During the performance period of this project, conventional in-situ laser based monitors and thick film ceramic ammonia sensors have been introduced and have gained acceptance in real-time feed-forward control for this application.

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1. Introduction

Overview

In this program, we proposed to demonstrate a compact, rugged, low-cost ammonia sensor with better than ±0.2 ppmv lower detection limit and resolution. This sensor would measure the infrared absorbance of ammonia at 1527 nm to determine concentration. Key features of this system are 1) a electronically-tunable, wavelength-agile diode laser-pumped fiber laser, 2) a unique, low-cost folded path optical cell, and 3) an InGaAs photodiode (light detector). The sensor would be designed to make *in situ* measurements of ammonia in flue gas just downstream from the catalyst. It would operate at pressures in the range 1-3 atm and temperatures up to 500°C and have ~1 sec response time. We designed it so that high levels of water vapor or ash in the flue gas would not affect the measured response to ammonia. In fact, this wavelength was chosen because of all of the IR absorbance wavelengths for ammonia, this has the least interference from water vapor and carbon dioxide.

This report presents the results of the program including the development of the sensor and its performance in measuring ammonia.

Background

Increasing concerns over air quality and new regulations have and will force thousands of power plants and other such large combustion furnaces to install NOx emissions control systems by the end of 2007. One proven method of reducing NOx emissions is Selective Catalyst Reduction (SCR) in which a reducing agent, usually ammonia, is added to the combustion gas stream. The ammonia reduces any NO present according to the reaction

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (1)$$

The catalysts used to promote these reduction reactions are usually titanium and vanadium oxides formed as honeycomb-shaped metal or ceramic plates and operated at temperatures of 370-425°C (700-800°F) for best catalytic efficiency.[1] The ammonia is typically injected downstream from the combustion chamber and upstream of the catalyst grid.

Often, there is incomplete mixing of the ammonia with NOx or too much ammonia is injected and some escapes past the catalyst and into the atmosphere. This is called ammonia slip. Ammonia slip can also be the result of poor temperature control at the ammonia injection point or high fly ash concentrations in the flue gas. Ammonia slip rates start at very low levels and increase over time with decreasing catalytic activity, which can be a result of simple aging of the catalyst or fouling. In fact, the best indicator of a loss of catalytic activity is an increase in ammonia slip.[2]
Since ammonia is considered a toxic emission and a contributor to ozone depletion, it is desirable to keep fugitive ammonia emissions to a minimum. Excess ammonia injection can also result in the formation of ammonium sulfate or bisulfate which can foul air preheater surfaces making them less efficient and promote corrosion.[3] It contaminates fly ash, giving it a strong odor and preventing the commercial sale of the ash. Excess ammonia can also increase exhaust opacity beyond regulatory limits. From a process point of view, excess use of ammonia results in loss of efficiency and added cost. What is

needed is a reliable, sensitive, low-cost ammonia sensor which can be used as part of a closed-loop feedback control system to limit ammonia slip.

Figure 1 shows a schematic of the sensor as proposed. A 1W diode laser operating at 980 nm pumps the erbium (Er^{3+}) -doped fiber. Er^{3+}-doped fibers can be tuned over the range 1525 nm – 1575 nm. A piezoelectric element stretches the fiber changing the cavity length of the fiber, thereby tuning the wavelength. The light is split, one part going to a reference detector and the other passing through the gas sample and falling on the signal detector. The reference detector allows us to compensate for any temporal fluctuations in the output of the laser. The detectors are standard InGaAs photodiodes. The ratio of the signals gives the absorbance due to ammonia in the sample.

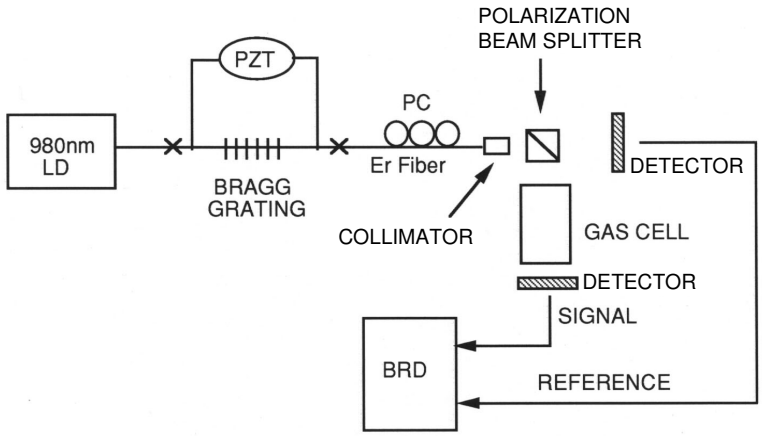

Figure 1 *Schematic illustration of fiber-laser ammonia sensor. A diode laser operating at 980 nm pumps the Er^{3+}-doped fiber. A piezoelectric element changes the cavity length of the fiber, thereby tuning the wavelength. The light is split, one part going to a reference detector and the other passing through the gas sample and falling on the signal detector. The detectors are InGaAs photodiodes. The ratio of the signals gives the absorbance due to ammonia in the sample.*

This approach has several advantages:

- The tunable fiber laser is more rugged and less expensive than say a tunable, external cavity 1.5 μm diode laser.
- Our folded-path optical cell is already demonstrated to withstand moist (90% RH), high temperature (>200°C) environments and can be made to withstand the higher temperature environment inside the SCR. Further, it is designed to be manufactured at low cost.
- Fiber coupling to the sample cell allows the diode laser, detectors and electronics to be kept in a safe, room temperature environment even as we are measuring corrosive, high temperature gases *in situ*.

These features combined will yield real-time measurements of ammonia concentration in the SCR unit and enable closed loop feedback control to achieve maximum reduction of NOx and ammonia emissions.

Some attempts to control ammonia slip have been made by using inlet and outlet NOx measurements in a feedback control scheme. However, the currently used chemiluminescence measurement method can only measure near room temperature gas, so the gas must be extracted from the exhaust stream and cooled before measurement. This introduces a 5-10 minute lag time which makes this measurement method unsuitable for closed loop feedback control. What's more, a recent survey of installed NOx CEMS found that 75% failed bias tests.[4] Other evaluations of chemiluminescence CEMS have shown uncertainty in the measured NOx level of up to ±20% for levels of 30 ppmv or more and up to ±6 ppmv (at O_2 concentration of 15 %) for concentrations below 30 ppmv.[5] These errors can result in high levels of ammonia slip which may not be noticed until significant fouling of the air preheater and other downstream equipment has occurred.[6]

The impacts of poor ammonia slip control can be significant:

Air heater fouling
At low ammonia slip (< 2ppm), units may run for 6-12 months before needing to wash air heaters. At slip concentrations above 10 ppm, air heater washing may be required every 2 weeks to 3 months.[7]

Increased costs
Reducing ammonia slip from 5 ppmv to 2 ppmv requires 20-30% more catalyst, $8/kWe higher capital cost, and 0.10 mills/kWh higher operating cost.[8]

Fly ash contamination
Slip values of 2ppmv yield fly ash ammonia concentrations of ~100 ppmw. Utilities have reported that at least 2.7 million tons of fly ash may be rendered unusable for pozzolan markets due to ammonia contamination. This represents 30% of the 9 million tons of fly ash used in cement and concrete applications in the USA in 1997. An additional 1.4 million tons of fly ash would be rendered unusable for applications other than cement and concrete applications. In total, more than 3 million tons of fly ash would be rendered unusable for any application and would require disposal. This represents 21% of the total ash currently used in the USA.[9]

Accurate measurements of ammonia concentration in such a harsh environment and at such low levels does present us with some measurement challenges:

Sampling
- The gas stream has high water content, other corrosive and reactive gases may be present.
- Particulate levels may be high.
- Ammonia may react with ash, SO_2/SO_3, water and chlorides present in the sample volume

- Temperatures are high enough (340 C/650 F) to present problems with most analytical techniques.
- Typical sample preparation for the chemiluminsecence CEMS is to remove, cool, dry and filter the sample. However, ammonia may continue to react with any NOx present on its way to the sensor. Cooling or drying will remove ammonia since ammonia is reactive with water. Filtering can create fouling, reaction and maintenance issues.

Analysis

- Water levels are high compared to ammonia, possibly leading to interference if water has nearby absorbance lines.
- The process stream is a complex mixture, difficult to separate the components, again possibly leading to interference from one or more of the various molecules present.
- Ammonia levels are low, so a lower detection limit of 0.1 ppmv or better is desired.
- The process can change rapidly so fast response time is essential.
- The gas can be corrosive, particularly to wetted parts.
- High dust levels can impede optical measurements.

2. TECHNICAL APPROACH

Our technical approach to ammonia detection in this challenging application was to address all of the sampling and analysis issues listed. The basic approach was straightforward. We would construct a prototype ammonia sensor consisting of a diode pumped fiber laser, electronically tuned to scan across one of the absorbance lines of ammonia near 1530 nm. The sensor would incorporate our new, low-cost folded path optical cell which would increase sensitivity to low ammonia concentrations and would be robust enough to withstand the high temperature, corrosive environment inside the SCR. This would enable real-time measurements of ammonia and subsequent closed loop feedback control. The goal was to demonstrate sensitivity down to an expected lower detection limit (LDL) of 0.2 ppmv or better both in the laboratory and in tests on an actual SCR unit at West Virginia University's Engine Test Facility.

Our light source is a diode laser-pumped fiber laser. In many ways, this is similar to the Er^{3+}-doped fiber amplifiers used to boost 1.5 μm fiber optic telecommunications signals. The fiber used for our laser is made in the same way and from the same materials as Er-doped telecommunications silica fibers. Er^{3+}-doped fibers have broadly tunable output from 1525 nm to 1575 nm which matches well with the ammonia absorbance at 1527 nm. With Bragg grating mirrors etched into both ends of a short piece of fiber to form an optical cavity, the fiber acts as an optical gain medium, in other words, a laser. This gain region can be optically excited or pumped by another light source. In our case, the Er^{3+} ions in the glass can be optically pumped with a 980 nm diode laser. These diode lasers are readily available and relatively inexpensive in quantity.

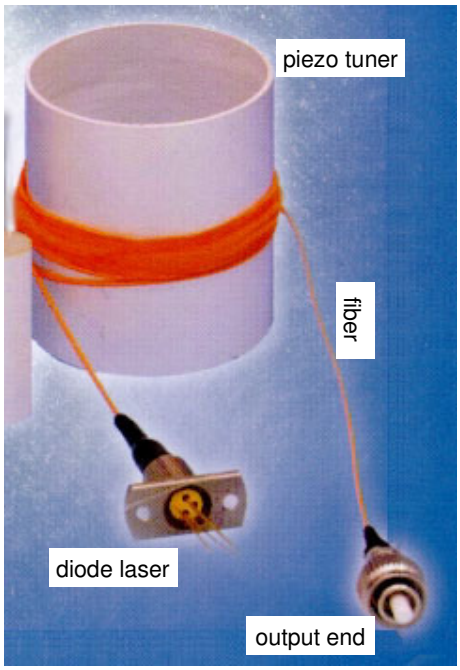

Figure 2 *A piezoelectric cylinder with a fiber laser wrapped around it. Applying a voltage to the cylinder changes its diameter and the laser's wavelength.*

The original program plan called for tuning the output wavelength of the fiber laser with a piezoelectric tuner which stretches the fiber. By stretching the fiber, we change the length of the optical cavity and the resulting resonant emission wavelength. One way to do this is to wind the fiber around a cylinder made from piezoelectric material like lead zirconate titanate (PZT), as shown in Figure 2. When an electric field is applied to the PZT, it expands by up to one percent, depending on the strength of the field. Therefore, as the cylinder increases in diameter, the fiber is stretched and the wavelength shifts. The shift can be as many as 10 or 20 nm from the nominal fiber wavelength.

We selected 1527 nm (6548.5 cm^{-1}) as the measurement wavelength because as we can see in Figure 3, there is no interference from either water vapor or carbon dioxide (CO_2) at this wavelength.[10] This is key since both are expected to be in high concentrations in the flue gas. The principle of the measurement is to tune the laser to a wavelength just short of one of the absorbance lines of ammonia, as shown in the figure. Then by stretching the fiber, we can tune the wavelength through the absorption line. The change in intensity as the wavelength tunes through the absorbance line is related to the concentration of ammonia through Beer's law. This method of gas sensing is variously called wavelength modulation spectroscopy by some and frequency modulation spectroscopy by others.

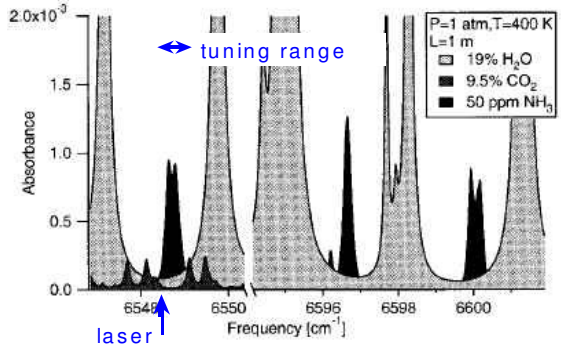

Figure 3 *Ammonia (50 ppmv) absorbance near 1.5 μm, shown with high concentrations of interferents water vapor and CO_2. The output from the fiber laser is tuned to a wavelength just short of one of ammonia's strong absorbance lines. Then stretching the fiber tunes the laser through the absorbance line.*

The program plan called for the tunable fiber laser to be fabricated and tested by Prof Ted Morse's group from the Laboratory for Lightwave Technology at the Boston University Photonics Center. This group has extensive experience fabricating rare earth-doped fiber lasers and they have already shown gas sensing using similar lasers tuned for nitric oxide (NO) absorbance as well as acetylene. Tuning the laser across

an absorption, this way, gives a signal like that shown in Figure 4.

Since the gain of rare earth doped lasers depends on the wavelength, that is, the intensity of our laser will depend on the wavelength it is tuned to, output from the fiber laser will be split. One part will go directly to a photodiode which will monitor any intensity variations from the laser itself and give us a reference with which to compensate for such variations. The other will pass through the sample chamber falling on another photodiode. The ratio of this signal to the reference gives a signal due only to absorbance in the chamber. Because we carefully selected the measurement wavelength to avoid interference from water vapor and CO_2, as well as NOx and all other compounds expected to be in the exhaust stream, the only thing besides ammonia which will be able to reduce the transmitted light intensity is soot particulates in the gas or a build-up of residue on the optical surfaces exposed to the sample. Over the small tuning range we will be using, any scattering from soot or deposits is expected to be the same for all wavelengths. Once we compensate for laser intensity vs. wavelength using the reference photodiode, any absorption must be due to ammonia.

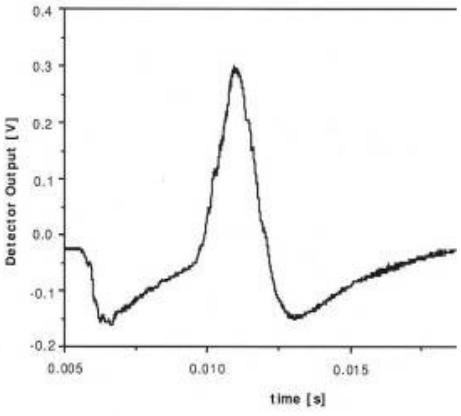

Figure 4 *Tuning the fiber laser through an absorbance line yields a signal proportional to the gas concentration.*

Since the ammonia absorbance near 1.5 μm is an overtone of a fundamental vibrational resonance, it a relatively weak IR absorption. We will need a relatively long optical path therefore to obtain a measurable absorbance. For this reason, we have developed a folded path optical cell as shown in figure 5. Currently, we are testing this optical cavity in conjunction with a CO sensor we are developing for a major automotive manufacturer. With the path length afforded by this sample chamber, we are achieving sensitivity of ~3 ppmv CO (Figures 6, 7). The added discrimination from a narrow laser line should enable us to achieve 0.2 ppmv lower detection limit.

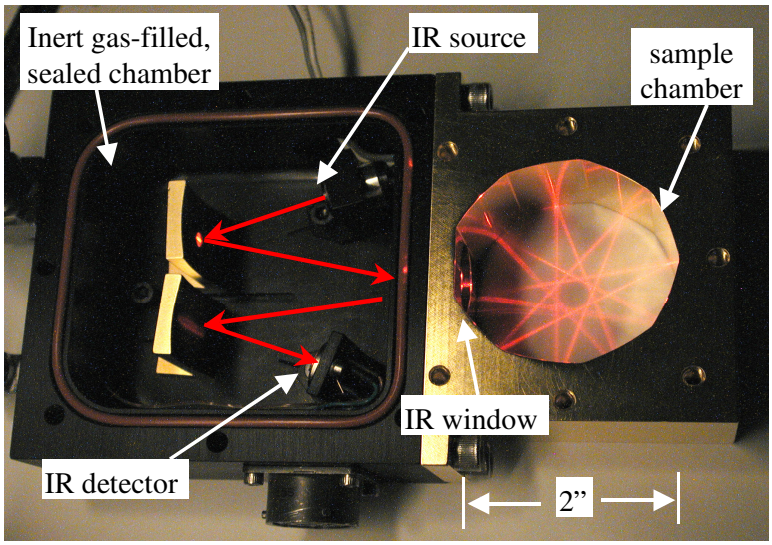

Figure 5 *IOI's folded path optical cell used to obtain increased path length in a small volume when needed for low concentrations or weak absorbers like CO. The configuration shown achieves a 45 cm (18-inch) path length in a 2-inch diameter x 1-inch high volume.*

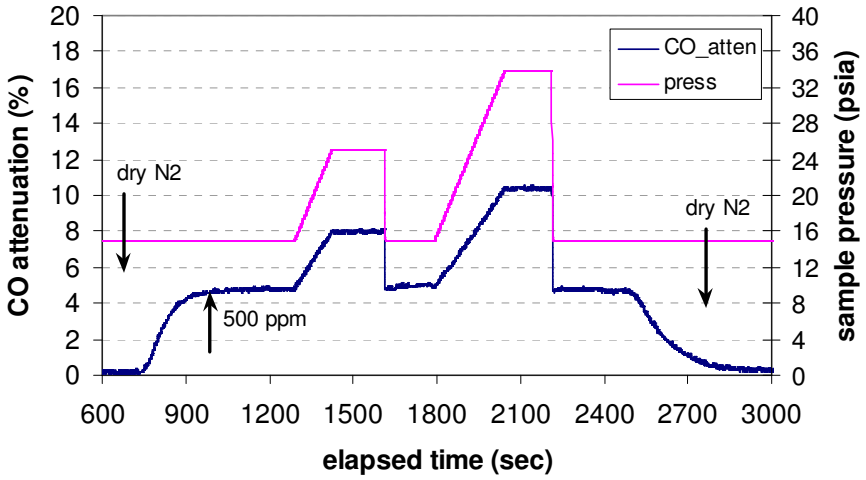

Figure 6 *Measured data for carbon monoxide showing signal-to-noise of ~75 which leads to a sensitivity of ± 7 ppm. This data is for a 200 msec response time. With slower response time (longer averaging) the sensitivity improves as shown below.*

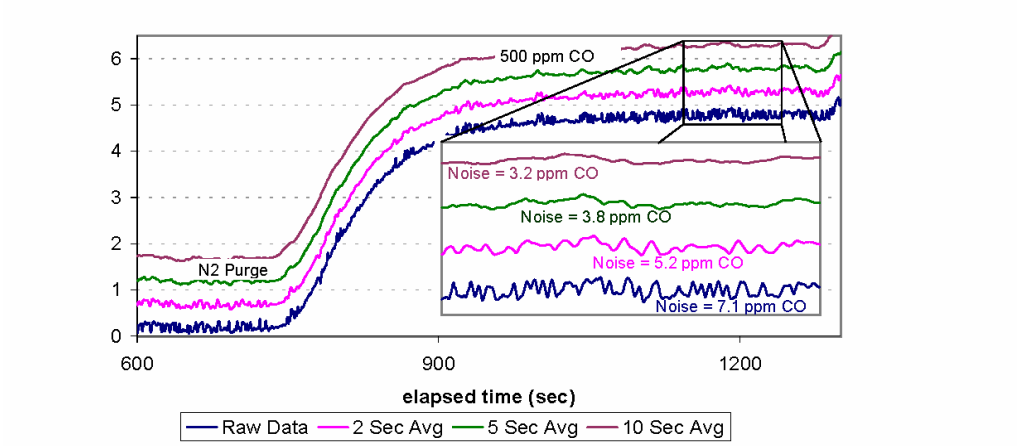

Figure 7 *Signal-to-noise reduction and improved sensitivity achieved with longer integration times. Improved sensitivity for low concentrations will also result from an increased optical path length.*

As constructed, the prototypes like the one in figure 5 were made from aluminum (black parts of box) and stainless steel plated with gold (mirrors). We have shown this to be capable of operating in relatively clean, water-saturated gas at temperatures up to 200°C and pressures up to 3 atm. There is no reason to think it would not withstand the slightly higher temperature of the SCR environment. However, we were concerned about corrosion or fouling from heavy hydrocarbons and byproducts like ammonium sulfate. As part of our technical effort, we performed long-term tests of various materials of construction by placing them in the flue of an actual boiler or stationary diesel engine. We planned to test stainless steel, kovar and aluminum as possible materials for the body of the sample chamber as well as gold, nickel, and a dielectric stack Bragg reflector constructed of materials like alumina and silica for the mirror surfaces. We would select the combination least susceptible to fouling in this harsh environment.

One of the aspects of our approach that makes it so robust is that we can perform an *in situ*, real-time measurement with only the body and mirrors of the sample chamber exposed to the harsh environment of the flue. Using an optical fiber to couple to the sample chamber allows us to place the rest of the measurement equipment (the laser, the detectors, the electronics) up to a few feet away in a relatively cool and comparatively benign atmosphere. With this design, we also avoid any ancillary equipment which may be needed to pump out a sample of the flue gas and cool it before making the measurement.

Technical Approach Synopsis

The overall program goal is to demonstrate a compact, rugged, low-cost ammonia sensor with better than ±0.2 ppmv lower detection limit and resolution. To achieve this goal we set the following objectives.

1 Fabricate a diode laser pumped, Er^{3+}-doped, tunable fiber laser operating at 1525-1535 nm. This means obtaining the pump laser, the doped fiber, fabricating the Bragg mirrors on the fiber laser, and obtaining the piezoelectric actuator to stretch the fiber.
2 Select materials of construction for the folded path optical cell that will withstand the high temperature, corrosive environment of the SCR.
3 Fabricate the folded path optical cell from the materials selected and obtain the other components needed such as the InGaAs photodiodes, electronics (A/D converter, etc.), fiber collimator, IR window, etc.
4 Assemble the prototype ammonia sensor from the above named components.
5 Write the software for the data reduction algorithm and user interface.
6 Calibrate the ammonia sensor on the lab bench. Determine the unit's lower detection limit, resolution, tuning range, etc.
7 Test the prototype sensor on a boiler or diesel engine equipped with an SCR. Establish response time, lower detection limit, operating lifetime before cleaning or replacement of the optical cell.
8 Determine the cost of building these ammonia sensors in volume for commercial customers.

3. WORK PLAN

This section presents the project work plan as put forth in the original proposal. The tasks listed above can be grouped into three phases. In phase 1, we will design and build the prototype ammonia sensor (tasks 1-6). In phase 2, we will test and calibrate its performance in the laboratory (task 7). Then finally, we will demonstrate the sensor on an SCR deNOx unit on a large stationary boiler or engine.

Task 1 – Establish design specifications for ammonia sensor

We will begin by surveying a number of potential customers in order to clarify their expectations for sensor performance range, repeatability, and ambient operating conditions. The box on the next page presents an excerpt from a preliminary set of specifications prepared by us for another type of sensor for monitoring indoor air quality. We will establish similar specifications for the ammonia sensor. With these specifications, we will establish the design requirements for the sensor including optical path length, sensor response time, measurement frequency (continuous, hourly, daily?), and power limitations.

Our expectation is that the sensor we have outlined - the tunable fiber laser, along with the hardened sample chamber and the wavelength modulation technique - will be compatible with most customer requirements.

While we are talking to potential customers, we will also determine which ones may contribute to the development of this sensor by investment of money or more likely time… time to test and evaluate the prototype and give us feedback and data on the sensor's performance in their SCR units. We have already received expressions of interest from at least 2 potential customers. However, at the moment they'd prefer that their interest be treated confidentially.

Once the design specifications have been finalized, we will begin assembly of the sensor to meet those specs.

Task 2 – Fabricate a diode laser pumped, Er-doped tunable fiber laser

The tunable fiber laser will be made by our collaborators at the Laboratory for Lightwave Technology at Boston University's Photonics Center. The director of the laboratory is Prof. Ted Morse who is well known as a researcher in fiber optic technology. The laboratory has everything needed to assemble the tunable fiber laser. It is equipped with CVD furnaces with which to make their own rare earth-doped fiber preforms as well as a drawing tower with which to make the fibers.

Once the doped fibers have been prepared, Bragg grating mirrors will be etched into the fiber to define the laser cavity length. The fibers will then be coated with a polymer for protection.

The fiber will be joined to a fiber-pigtailed diode laser which will be used to pump the fiber. The Laboratory will also be responsible for winding the fiber around the piezoelectric actuator which will be used to stretch the fiber and thereby tune the output wavelength.

Finally, the tunable fiber laser will be fully tested to ensure that it yields narrow-band single mode output of the needed wavelength range of 1525-1535 nm. They will measure the optical conversion efficiency of pump laser power to fiber output power and they will calibrate output wavelength vs. voltage applied to the piezoelectric actuator.

The fiber laser will be delivered to Ion Optics along with all test results as well as instructions for the proper handling of the laser.

Task 3 – Select materials of construction for the folded path optical cell

We will run tests to determine whether our current stainless steel optical cell with gold mirrors can withstand the harsh environment of the SCR. We will conduct these tests in conjunction with interested potential customers and our collaborators at the Engine and Emissions Research Center in the Dept. of Mechanical & Aerospace Engineering at West Virginia University. This DOE and EPA-sponsored group is assisting us with the development of a diesel engine exhaust analyzer on another program.[11] Their facility is equipped with several large diesel engines as well as state-of-the-art engine test equipment.

The experimental protocol will be to prepare mirror blanks, for example gold on stainless steel, and place them in the exhaust pipe of an engine at a point where it would experience the same temperatures and exhaust gases to be found in a typical SCR unit. At periodic intervals, the pieces will be removed, thoroughly inspected for any signs of fouling, corrosion, or other modes of deterioration. We will also measure the absolute reflectance of the mirrors using an FTIR spectrometer they have on-site. Any signs of deterioration will be documented.

We have identified a number of other materials to mitigate the risk that the corrosive gases in the SCR might damage the optical. For the body of the optical cell, kovar and aluminum may be suitable alternatives to stainless steel. Kovar, an iron-cobalt-nickel alloy, is often used in applications where resistance to temperature and corrosion as well as low thermal expansion are important. Aluminum of course is a light-weight, corrosion resistant material that is limited to temperatures below 600°C. It has the advantage however that it is easy to machine and can even be cast or stamped to form the needed shape. For the IR mirror coating, nickel is possible alternative to gold. It has high reflectance, a high melting point, and it resists corrosion. If neither will sustain the SCR environment well, we may try a dielectric mirror instead. Alternating thin layers of dielectric materials like alumina, silica, and silicon nitride will form a Bragg reflector like that shown in Figure 8. Here alternating layers of silicon nitride and silicon-rich silicon nitride were deposited (by our collaborators at Boston U.) to form a narrow-band reflector for 840 nm.[12]

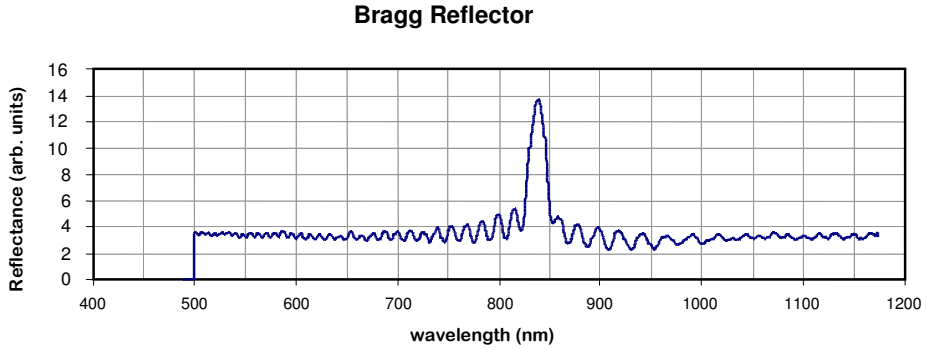

Figure 8 *Multi-wavelength reflectance spectrum measured in situ for a Bragg reflector deposited on a quartz window. The Bragg mirror consists of 60 pairs of l/4 layers consisting of silicon nitride (n = 1.8, d = 116 nm) and silicon-rich silicon nitride (n ≈ 1.9, d = 110 nm). Reflectance peak occurs at 840.7 nm with FWHM = 17.8 nm.*

The results for this task should be a clear indication which combination of materials is best to withstand the harsh environment inside the SCR unit.

Task 4 – Fabricate folded path optical cell and other components

Once the best materials for the folded path cell have been identified, we will fabricate three of them. Any machining will be done by nearby machine shops we use frequently to

make precision parts. Mirror coatings will be deposited by outside vendors who have demonstrated their capabilities on previous projects for us.

As part of this task, we will also obtain whatever other components may be needed to build a fully functional ammonia sensor. For example, we expect to need several InGaAs photodiodes to detect the 1530 nm light from the fiber. A preamp for the photodiode along with an A/D card so the signal can be logged with a computer will be needed. Additionally, we will need optical windows and fittings to attach our optical cell to the flue in the proper position.

Task 5 – Assemble the prototype ammonia sensor

Once the needed components have been obtained, we will assemble the prototype. The tunable fiber laser (delivered by Boston Univ.) and the InGaAs detectors will be fiber-coupled to the ruggedized folded path optical cell. All wiring will be completed, *e.g.* power supply to diode pump laser, detectors to preamp, preamp to computers, etc. The sensor will be turned on and nominal operation (power on ➔ measurable optical signal) verified before calibration and testing are performed.

Task 6 – Write the data reduction software

At Ion Optics we have a lot of experience developing prototype gas sensors. We always use LabView™ software to control the prototype and reduce the measured data because of its power and flexibility and because of the ease with which it can be changed while tests are continuing.[13]

The software to operate and control the ammonia sensor will have three main functions. First, it will control the output wavelength of the fiber laser by commanding the voltage applied to the piezoelectric actuator that stretches the fiber. Piezoelectrics often exhibit hysteresis, so it is important to know whether the voltage is increasing or decreasing, we have previously seen that a simple polynomial will relate voltage to output wavelength. Second, the computer will record and log the measured output from the photodiodes and then calculate the absorbance due to ammonia. Finally, the software will convert ammonia absorbance to ammonia concentration based on Beer's law and calibration data from task 7.

Task 7 – Calibrate the ammonia sensor on the lab bench

Ion Optics will measure the precision, accuracy, and sensitivity of the ammonia sensor on the lab bench under controlled test conditions. We have our own computerized gas delivery system (see IOI facilities attachment) capable of diluting the gas in a cylinder by up to 10,000:1. Data from sensors is also gathered by automated systems. Ultimately accuracy will be tested with cylinders of well-characterized gas mixtures, *e.g.* 1000 ppmv ammonia in nitrogen. Routine tests will use diluted mixtures, with concentrations adjusted by electronic mass flow meters (accuracy to ±0.5%). True zero concentration can be assured for these tests by pumping to high vacuum and purging with electronic grade nitrogen (total impurity level less than 0.5ppm and most of that would be water vapor). With these tests, we will establish the lower detection limit and resolution of our prototype as functions of gas cell temperature (50-450°C), pressure (1-3 atm), and interferent concentration (both water vapor and CO_2) up to 20%. We will also establish

any dependence there may be on wavelength tuning modulation amplitude or frequency. This will allow us to establish the algorithm to convert measured ammonia absorbance to ammonia concentration over a wide range of operating conditions.

Task 8 – Test the prototype sensor on a boiler

Following calibration and bench-top testing of the ammonia sensor under task 7, we will place the sensor in the deNOx unit of a power plant or diesel engine. We will again work with our collaborators at West Virginia University who have several SCR units for engines on-site. We will run the sensor continuously for up to three months, all the while recording measured ammonia readings. As before, the optics will be inspected periodically for any signs of deterioration due to the harsh environment.

Based on confidential communications, we believe at least one potential customer will also be happy to have us test our sensor in their power plant, as long as we can schedule the installation and removal for times when they are performing routine maintenance and they won't have to shut down the system especially for us.

The most important finding to glean from these tests is how real flue gas and especially soot affects the ammonia measurement. Is the lower detection limit significantly impacted by high soot levels? Do the optics become coated or otherwise less reflective as a result of being exposed to actual exhaust gas? If the optics do become coated, we will determine the rate of deterioration (vs. hours of operation or amount of fuel used). We will also attempt to develop a cleaning procedure and a suggested cleaning schedule.

Task 9 – Determine the cost of production

Ion Optics' business model is to build integrated gas sensors that are smaller, more sensitive and less expensive than any other infrared gas sensor commercially available. We expect the tunable fiber laser to be simpler and substantially less expensive than any tunable external cavity diode laser. Long path optical cells that are commercially available now cost thousands of dollars. We have estimates that show we can build our sample chamber for a few hundreds. Under this task, we will submit written specifications to multiple vendors and obtain written cost estimates for fabricating this ammonia sensor in quantities of 10, 100 and 1000 units. Our target is a sub $1000 price for the entire sensor.

Task 10 - Reporting

The original program as planned was expected to last 18 months. Monthly progress reports and a final technical report were to be submitted.

4. WORK PERFORMED

This section details the work performed during the course of the program.

Establish design specifications for ammonia sensor

We began by obtaining information from a number of sources concerned with ammonia slip issues. Sources included engineers at Cummins Engines and especially collaborators from the Alternate Fuels, Engines, and Emissions Center at West Virginia University. These sources have extensive experience measuring engine emissions and some

experience with urea-based deNOx systems that generate ammonia. Our target operating conditions for this ammonia sensor are then by consensus:

Exhaust gas:

flow rate	10 – 800 slpm
temperature range	50 – 500 C
pressure	1 – 3 atm
ammonia concentration	0.1 – 50 ppm
water vapor concentration	100% RH, saturated

These requirements mean that the sample measurement chamber must be robust to handle the raw exhaust or we must siphon off a portion of exhaust and pre-condition it to reduce temperature and remove water vapor. We plan to make the sample chamber robust enough to handle the raw exhaust, and if we have difficulty making the measurement, our collaborators at WVU have the experience and equipment to condition the exhaust sample for measurement.

Figure 1 above showed the original schematic illustration of our proposed sensor. Figure 9 is an improved version of that drawing. It shows a 1W diode laser operating at 980 nm pumping the erbium (Er^{3+}) - doped fiber. As mentioned above, Er^{3+}-doped fibers can be tuned over the range 1525 nm – 1575 nm. A piezoelectric element stretches the fiber changing the cavity length of the fiber, thereby tuning the wavelength. The light is split, one part going to a reference detector and the other passing through the gas sample and falling on the signal detector. The reference detector allows us to compensate for any temporal fluctuations in the output of the laser. The detectors are standard InGaAs photodiodes in a configuration known as a balanced ratiometric detector (BRD) which simplifies taking the ratio of the two signals.

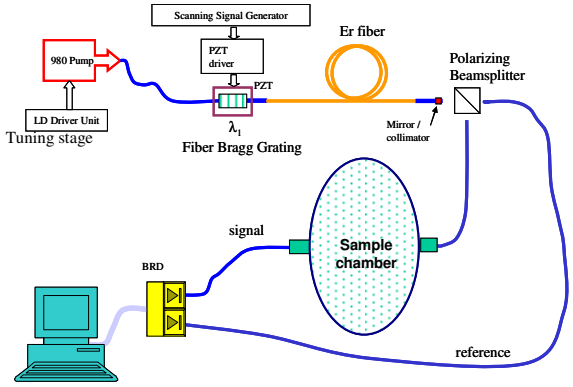

Figure 9 *Schematic illustration of original fiber-laser ammonia sensor design. A diode laser operating at 980 nm pumps the Er^{3+}-doped fiber. A piezoelectric element changes the cavity length of the fiber, thereby tuning the wavelength. The light is split, one part going to a reference detector and the other passing through the gas sample and falling on the signal detector. The detectors are InGaAs photodiodes. The ratio of the signals gives the ammonia absorbance.*

With Prof. Ted Morse and co-workers at Boston University's Photonics Center, we established requirements for the tunable fiber laser for this program:

Diode-pumped fiber laser

fiber dopant	Er^{+3}
wavelength range	1525 – 1565 nm
fiber exit facet integrated power	> 10 mW

Detector Properties

Detector type	InGaAs PIN
Responsivity @ 1550 nm	0.90 A/W
Noise current	< 0.02 $pA/\sqrt{Hz}$

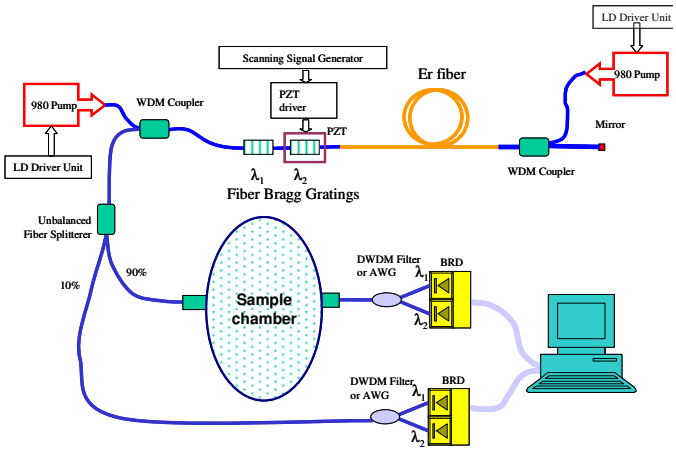

Figure 10 *Dual-wavelength fiber-laser ammonia sensor. Here we use two fiber Bragg gratings, one tunable by a piezoelectric element, one fixed. We also add a second pump laser to increase output power. The fiber laser output light containing both wavelengths is split, one part going to a reference leg and the other passing through the gas sample. Both reference and sample legs are divided into the two wavelengths and measured using the InGaAs photodiode balanced ratiometric detectors. The ratio of the reference leg signals allows us to compensate for scattering, interference and light source fluctuations.*

however can have a drawback, which is exactly what we observed: significant fluctuations or oscillation of output power distributed between the two wavelengths. This 'mode beating' is an instability that occurs when there is competition between the two allowed wavelengths for power. Changes in relative

While the laser in figure 9 is a useful and simple design, this sensor is not be able to compensate for non-ammonia-related changes in the sample chamber, *e.g.* dust in the air, water droplets/fog, contamination of sample chamber mirrors, etc. Hope Techonologies suggested a better design that can handle these interferences as shown in figure 10. Here we add a second, fixed reference wavelength (one that will not be absorbed by ammonia) which we can measure to monitor intensity reduction due to dust in the air sample or on the optical surfaces of the sample chamber.

In fact, our first layout for the as-built ammonia tunable fiber laser was this two wavelength design … and we were able to obtain dual wavelength output, as shown in figure 11. This design

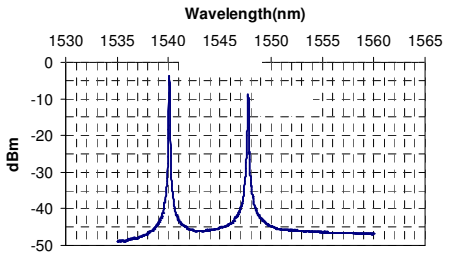

Figure 11 *Measured dual wavelength output from fiber laser depicted in figure 10.*

output power of the two wavelengths might look like signal from ammonia absorption. We could try to suppress this phenomenon by separating the two wavelengths into different fibers, as shown in Figure 12. However, this adds a minimum of $600 to the cost and was not the direction we wanted to take.

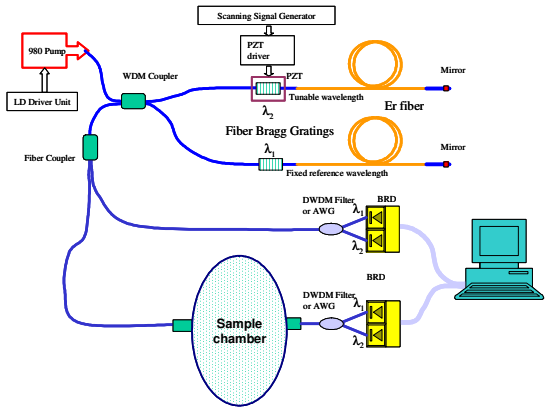

Figure 12 *Schematic illustration of dual-wavelength fiber-laser ammonia sensor similar to figure 10 but with separately pumped Er-doped fibers generating independent wavelengths.*

To overcome the mode-beating, our collaborators at Hope Technologies instead recommended a dual wavelength design which obtains the reference wavelength from the pump laser itself instead of the Er-doped fiber. This suppressed the instability we saw in the output of the previous (figure 10) design. We replaced the 980 nm pump laser with a 1480 nm pump. It is less efficient at optically pumping the Er than 980 nm, but it was good enough to obtain ~20 mW 1.5 ¤m fiber output given a 200 mW diode laser pump power. The layout is shown in figure 13. Again we have added a reference leg that we can use to subtract any laser noise. This additional reference leg contains a transmission cell with a fixed, known amount of ammonia as a reference. This is a method called gas correlation spectroscopy. It should give us the best sensitivity for ppm levels of ammonia.

An additional change in the final design is the replacement of the piezoelectric fiber-stretching tuning element with an alternative tuning element – a MEMS tunable filter, originally developed by CoreTek (now Bookham Technologies.) This is a fiber coupled device containing a small, fiber-coupled Fabry-Perot etalon as the tuning element. It has a wide tuning range (~1350 nm – 1600 nm) and

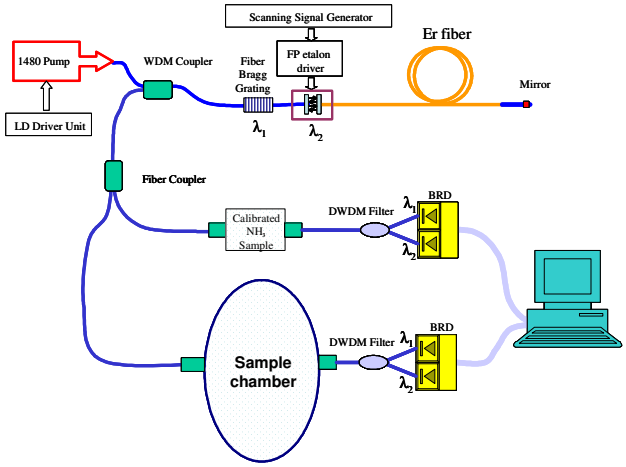

Figure 13 *Schematic illustration of final design of the dual-wavelength fiber-laser ammonia sensor. It is similar to earlier designs but with 1480 nm diode laser pump and reference wavelength.*

is highly responsive and repeatable.

Assemble the tunable fiber laser

All parts were ordered by and the laser was assembled by Hope Technologies, a spin-off from the Boston University Photonics Center. Upon completion, the output of the diode laser / fiber laser combination was measured with an Ando Q6312 Optical Spectrum Analyzer and is shown in figure 14.

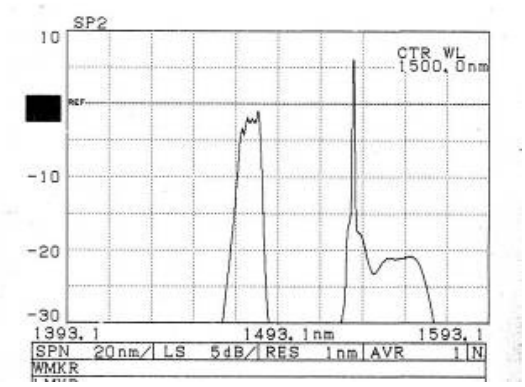

Figure 14 *Measured output from tunable fiber laser. The 1480 nm diode laser pump is clearly visible as is the 1530 nm Er-doped fiber emission. Notice that the fiber laser output is much more monochromatic (has smaller halfwidth) than the output of the diode pump laser.*

Upon testing the laser and verifying its performance, we accepted delivery from Hope Technologies and immediately undertook to place the fiber laser inside an instrument enclosure making it as compact and professional as possible. The result is a rugged package which can be taken into the field for on-site, on-engine measurements (front panel is shown in figure 15.)

Figure 15 *Tunable fiber laser as-packaged by IOI. Front panel display is part of laser diode driver and can select from diode laser current, temperature, output power, and thermoelectric (TE) cooler current.*

Initial testing was performed with an Ando optical spectrum analyzer, resulting in the measured spectrum shown in figure 14 above. The output power and wavelength of the

fiber laser were also measured as a function of voltage applied to the DC-DC amplifier driving the MEMS tunable filter. (Figure 16) Note that the wavelength can be swept from 1523 nm to 1567 nm and the output power varies repeatably only about 20% over the entire range.

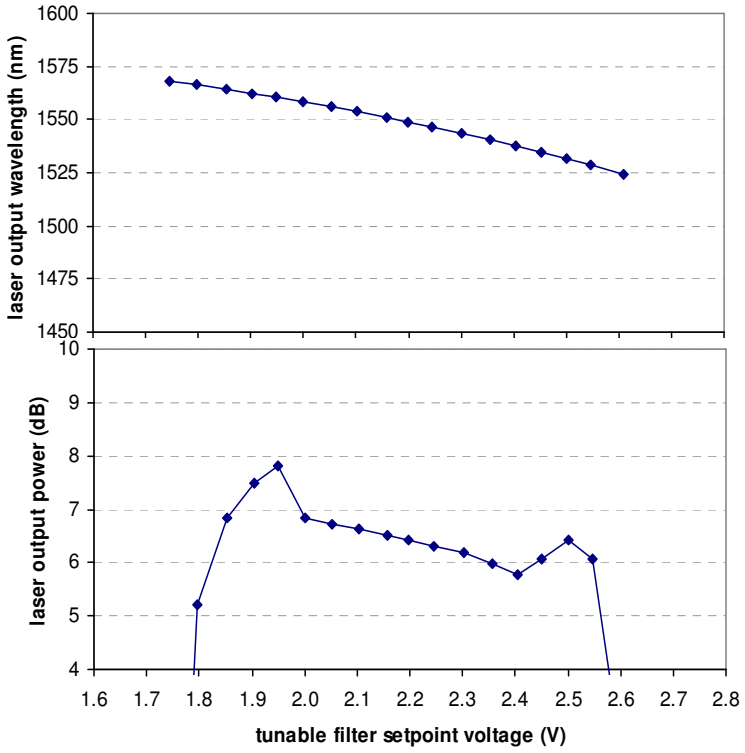

Figure 16 *Wavelength vs. applied voltage to tunable filter (top.) Output power vs. applied voltage (bottom.)*

Sample chamber design

The sample chamber needs to be robust enough to withstand the harsh environment (high temperature, soot, hydrocarbon and other gases) of the SCR. The original design consists of a sample cavity with a diameter of 2 inches with 9 mirror segments and an entrance aperture as shown in figure 17.

The mirror segments have a radius of curvature in the horizontal plane of the cavity R1 equaled to 2 inches. Rays are reflected by the mirror segments only once. The surfaces of the cavity are deposited with a light reflective coating, with the exception of at least one segment, which serves as a light transmissive window, for light entering and exiting

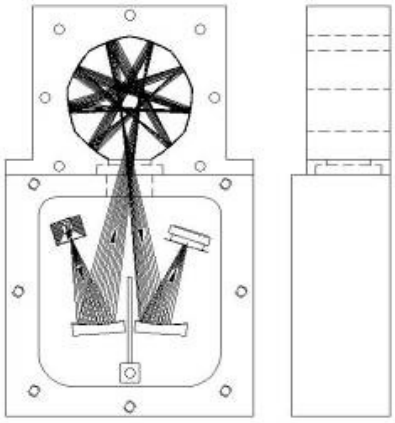

Figure 17 *Optical package and ray trace showing wide-angle, incoherent source and light path.*

the cavity. The light transmissive window may be made of sapphire, or other appropriate material (Ge, CaF_2, BaF_2, SiO_2 etc.) as dictated by the wavelength pass/cutoff requirements of the system. The geometry of the cavity serves to reflect incident light within the cavity, with the minimum number of reflections equal to the number of reflective surfaces. The radius of curvature of each arc acts to focus and re-image divergent light sources having radiant flux of wide angular extent (non-collimated), on each reflection, for efficient transmission of light, facilitating the use of commercial broadband, frequency distributed IR sources.

For a cavity diameter of 2 inches and flat vertical sides, the light path length is 18 inches, bouncing once from each segment, at about 11% throughput. Curvature on the longitudinal (vertical) direction of the cavity walls can improve both the throughput efficiency and output uniformity. Adding the vertical curvature could increase efficiency to 75% while maintaining the same path length. (Figure 18).

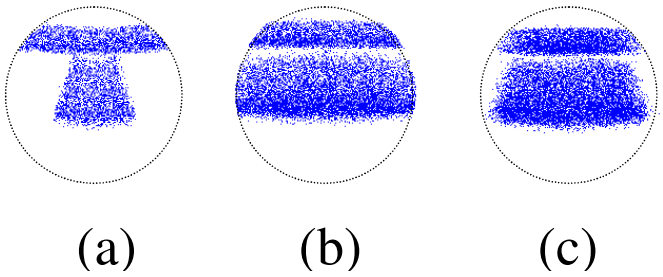

Figure 18 *Transmitted light power distribution on detector package using toroidal cavity optics with increasing vertical curvature. Case (a) is a flat vertical wall.*

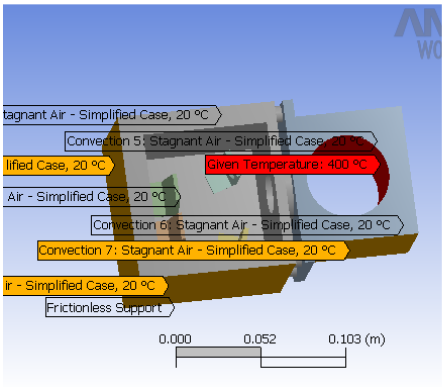

Figure 19 *Geometry and boundary conditions for baseline case (all metal) thermal model.*

Thermal design

Good thermal design is critical to our success. The exhaust in an SCR unit is expected to vary from a low of about 200C to a high of 400C. The sample chamber with the folded optical path

(like that shown above in figure 5) can be made from a high temperature material, for example stainless steel or Inconel or Hastelloy. However, the fiber and its collimator which we hope to place close to the sample chamber can only withstand temperatures up to about 150 C. To solve this issue we looked at various designs to reduce thermal conductance between the sample chamber and the external compartment which houses the mounting brackets for the fibers and their collimators.

In the initial modeling, figure 19, the "cell" was assumed to be stainless steel: the optics box and the inserts (mirrors and detector, and source) were assumed to be aluminum. The inside surface of the cell is set to 400 C and all external surfaces are assumed to be subject to static convection cooling in air, room temperature of 20 C and nominal heat transfer coefficient of about 5W/m^2. The contact surface between the optics box and the "cell" can slip sideways slightly along the plane but components are assumed to be in intimate thermal contact. Total stress is very small except at the point where the aluminum box touches the steel cell around the central optical port.

Minimum temperature in the baseline model was 365 C – static convection did little to reduce the temperature. Deformation was under 0.1 mm for most of the model but the design must still reduce the temperature of the optics box. Some of the design variations we looked at included an insulating optics box and thermal stand-offs between the modules. We chose Macor (machinable ceramic with a thermal expansion coefficient close to that of metals) for the optics block, with standoffs between the optics box and the cell. (Figure 20)

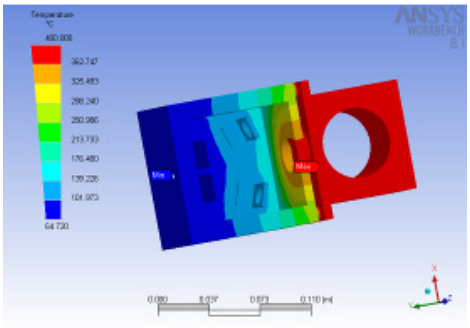

Figure *20* *Insulating design for optics housing. Temperatures in the optics module are dramatically lower, and can be brought still lower with forced air cooling on the case*

Fabrication

Machined parts were built and assembled. One particular integration issue was the question of protecting the mirrors. For the wavelengths we will be using (~1.5 μm), we can use the industry standard MgF_2-coated aluminum mirrors, provided the mirror temp does not exceed 450 C, where the quality of the aluminum mirror may start to degrade. Un-coated gold mirrors may also work. We conducted exposure tests on coupon (~ 1-inch square sample) of candidate coatings and determined that plated gold was adequate. We also examined potential passivation coating overlayers to provide additional protection for the gold first-reflection surfaces.

Laboratory calibration of sensor

We designed and built a small gas manifold with a stainless steel temperature controlled ammonia bubbler and separate exhaust tubing to vent the ammonia-bearing gas charge safely to a fume hood. Because of the flow rates achievable and the tubing length

required for safe handling of ammonia, the test manifold had a flush-out time of several minutes. While we expected to measure ammonia response with this set-up, the dead volume inherent in the manifold prevented meaningful measurements of response time.

Signals from both detectors and the built-in thermocouple gauge were read-out and recorded in real-time with LabView. The laser wavelength scans are clearly visible in the real-time LabView output (sawtooth wave structures, Figure 21.)

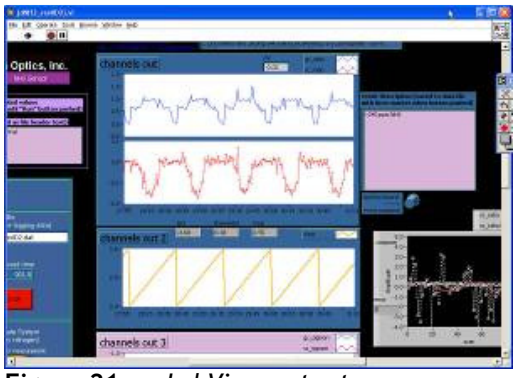

Figure 21 *LabView output screen capture of the unit in operation. Sawtooth wave structure is the underlying laser wavelength scanning operation. Ammonia concentration information is contained in the time history of the signal channel (blue trace) but must be deconvolved from aerosol scatter and temperature effects which are also contained in the guard channel (red.)*

The initial signal processing intent was to produce a difference spectrum between the two measurement channels and to rely on the wavelength specificity of the signal channel to provide an ammonia signal. The background clutter inherent in the system frustrated this algorithm, and we were not able to reliably recover a processed signal which represented ammonia concentration varying over time. To overcome this, we developed a software "lock-in" which the entire transmitted intensity for each of the measurement channels, time-gated on the laser sweep. This allowed us to recover an unambiguous ammonia signal. But it degraded the sensor's update rate to once every laser sweep (about 3 seconds.)

Output from the software lock-in is reported in arbitrary units, but clearly shows the turn-on and turn-off for ammonia vapor in the dilute test gas stream. (Figure 22)

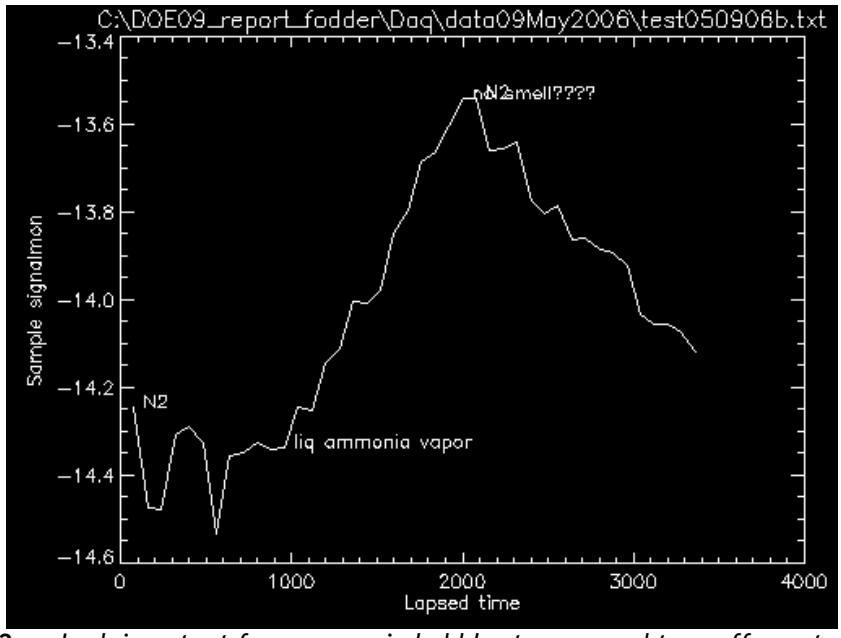

Figure 22 *Lock-in output from ammonia bubbler turn-on and turn-off events during initial lab testing. Oscillations during the initial N2 flow indicate a thermal noise limit for minimum-gas-concentration change measurements. We estimate that peak ammonia concentration at around 240ppm and the noise level is roughly 50 ppm ammonia.*

Test of sensor on SCR unit

Following further refinements in temperature stabilization, mechanical mounting, and signal processing, we mounted the complete sensor on an SCR exhaust port in the WVU engine lab. (Figure 23)

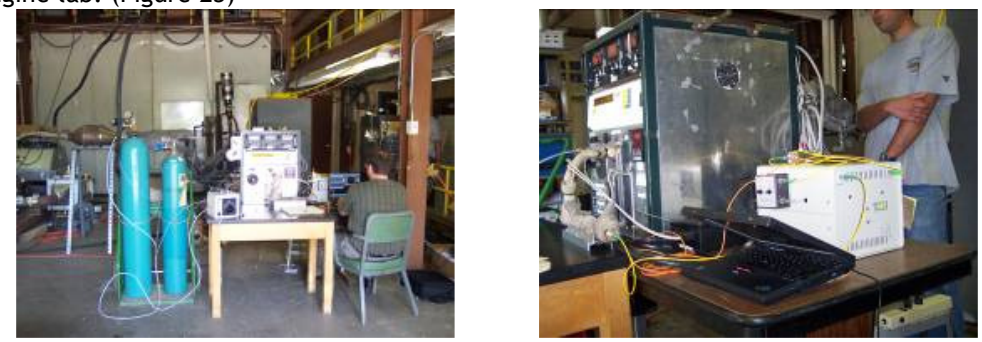

Figure 23 *Ammonia sensor set-up in the WVU engine lab.*

Temperature excursions in the actual gas stream caused significant measurement hysteresis as the sensor body successively heated and cooled. This appears in the data as a lag time (hundreds of seconds) between changes in the engine condition and changes is

the ammonia signatures. However we can still recover an unambiguous ammonia signal from the data. (Figure 24)

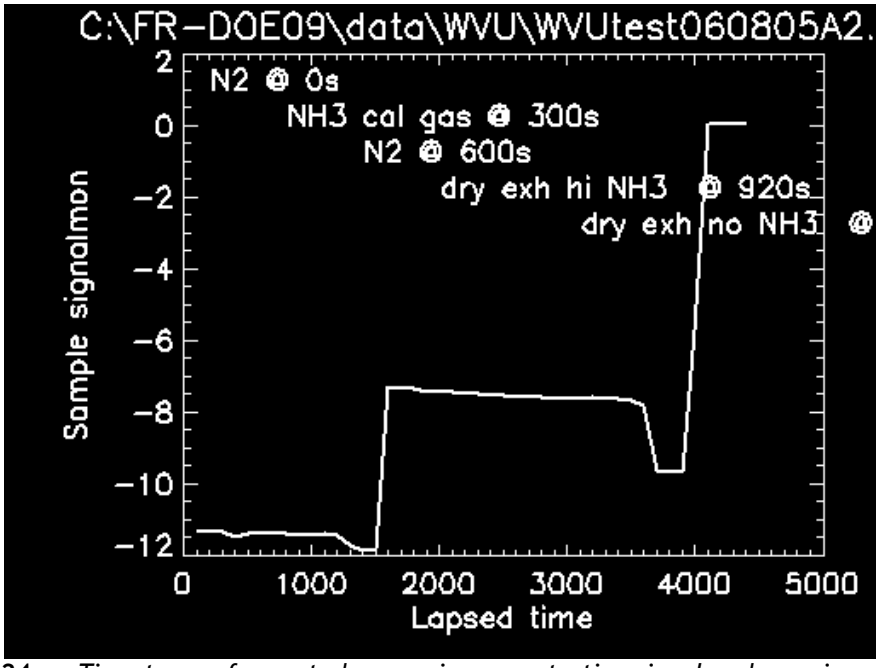

Figure 24 *Time trace of reported ammonia concentration signal under various engine operating conditions in the WVU engine lab.*

4. Conclusion and Summary

The useful sensitivity of the ammonia measurement is governed by signal to noise ratio (that is, the strength of the ammonia response divided by the sensor output fluctuation due to thermal and other ambient conditions.) As constructed, the dual channel ammonia sensor can detect ammonia under the designed operating conditions. But its useful sensitivity is far short of the goal of sensing changes less than 1 ppm. While this offers a promising start for a usable real-time control signal, the brassboard sensor does not yet provide the speed or sensitivity for real-time use in an industrial setting.

To pursue the goal of useful real-time feedback with this approach, the optical cavity will have to provide additional path length for enhanced absorption signal. At the same time, the laser wavelength scanning will need to operate much faster with a more robust, real-time signal processing architecture.

5. References

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[1] "De-NOx Source Monitoring - Ammonia Slip in Flue Gas", Analytical Specialties, Inc., www.analyzer.com, March 1999.

[2] *Current Practices for Monitoring Ammonia Slip from SCR Processes*, Mr. Ralf Sigling, Siemens KWU, Mr. Robert Johnson, Siemens Power Corp.

[3] Trevor Knittel, Analytical Specialties, Inc., private communication.

[4] Richard D. McRanie, RMB Consulting & Research, Inc., "Low Level NOx Measurements and Related Compliance Issues on Gas Turbine Combined Cycle Units", (2000).

[5] Wilfred S.Y. Hung and Alan Campbell, Solar Turbines Inc., "Uncertainty in Gas Turbine NOx Emission Measurements", EnergyPubs.com (1999).

[6] W. Scott Hinton, Hinton and Associates, "Advantages of the Optimized Operation of SCR Facilities", *1999 Conf. On Selective Catalytic and Non-Catalytic Reduction for NOx Control*.

[7] Control and Pollution Prevention Options for Ammonia Emissions, Control Technology Center, Information Transfer and Program Integration Division Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, April 1995.

[8] An Evaluation of the Proposed 37-State Seasonal NOx Control Program – Compliance Costs and Issues, Prepared for: The Center for Energy and Economic Development, Midwest Ozone Group, National Mining Association, prepared by: Thomas A. Hewson, John B. Stamberg, Energy Ventures Analysis, November 1995.

[9] Unintended Effects of EPA's Recent Ozone Transport Rule. Barry R. Stewart, American Coal Ash Association, Alexandria, VA 22314.

[10] M.E. Webber, *et al.*, *Appl. Opt.*, **40**, 2031 (2001).

[11] Dept. of Transportation, SBIR Phase 2 program, "Heavy-Duty Marine Diesel Emissions Rate Monitor", Contract no.: DTRS57-01-C-10043 (2001).

[12] James T. Daly, John A. Wollam, Fei Luo, Theodore F. Morse, Andreas Kussmaul, and Dan Pulver, "Multi-Spectral, Reflectance-Mode Fiber Optic Deposition Rate Monitor", *Proc. SPIE*, **3938**, 23-28 January 2000.

[13] LabView is a trademark of National Instruments, Austin, TX.